An Ultrasensitive Bio-surrogate for Nanoporous Filter Membrane Performance Metrology Directed towards Contamination Control in Microlithography Applications

Farhan Ahmad*[a], Barbara Mish[a], Jian Qiu[a], Amarnauth Singh[a], Rao Varanasi[b], Eilidh Bedford[a], Martin Smith[a]
[a]Center for Applied Material Science, Pall Corporation, 25 Harbor Park Drive, Port Washington, NY USA 11050; [b]Scientific and Laboratory Services Global Technical Support, Pall Corporation, 25 Harbor Park Drive, Port Washington, NY USA 11050

ABSTRACT

Contamination tolerances in semiconductor manufacturing processes have changed dramatically in the past two decades, reaching below 20 nm according to the guidelines of the International Technology Roadmap for Semiconductors. The move to narrower line widths drives the need for innovative filtration technologies that can achieve higher particle/contaminant removal performance resulting in cleaner process fluids. Nanoporous filter membrane metrology tools that have been the workhorse over the past decade are also now reaching limits. For example, nanoparticle (NP) challenge testing is commonly applied for assessing particle retention performance of filter membranes. Factors such as high NP size dispersity, low NP detection sensitivity, and high NP particle-filter affinity impose challenges in characterizing the next generation of nanoporous filter membranes.

*farhan_ahmad@pall.com; phone 516-801-9149; fax 516-801-9761; http://www.pall.com/

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We report a novel bio-surrogate, 5 nm DNA-dendrimer conjugate for evaluating particle retention performance of nanoporous filter membranes. A technique capable of single molecule detection is employed to detect sparse concentration of conjugate in filter permeate, providing >1000-fold higher detection sensitivity than any existing 5 nm-sized particle enumeration technique.This bio-surrogate also offers narrow size distribution, high stability and chemical tunability. This bio-surrogate can discriminate various sub-15 nm pore-rated nanoporous filter membranes based on their particle retention performance. Due to high bio-surrogate detection sensitivity, a lower challenge concentration of bio-surrogate (as compared to other NPs of this size) can be used for filter testing, providing a better representation of customer applications. This new method should provide better understanding of the next generation filter membranes for removing defect-causing contaminants from lithography processes.

Keywords: Filtration, nanoporous, filter membrane, nanoparticle, metrology, DNA-dendrimer conjugate, lithography, contaminant

1. INTRODUCTION

The semiconductor industry employs filtration technologies for removing contaminants from semiconductor manufacturing processes to reduce wafer defects and to improve yield. Contamination tolerances in photochemical manufacturing processes have changed dramatically in the past two decades, and have reached sub-20 nm sizes according to the guidelines of the International Technology Roadmap for Semiconductors[1]. The move to narrower line widths drives the need for innovative filtration technologies that can achieve higher particle/contaminant retention performance resulting in cleaner process fluids. Nanoporous filter membrane metrology tools that have been the workhorse over the past decade are also now reaching limits. Parallel development in nanoporous filter membranes and their retention performance metrology methods are required to meet future market demands. Nanoporous filter membranes are commonly characterized using porometry and nanoparticle (NP) challenge test methods[2]. Limitations of current porometry methods include a restriction to sub-15 nm pore-size, potential solvent-filter material interaction, and lack of direct retention performance evaluation. NP challenge testing methods for directly assessing particle retention of filter membrane have limitations in quantifying filter membrane performance due to low NP detection sensitivity, potentially high NP-filter affinity, and lack of size distribution assessment. Therefore, filter membrane challenge testing is commonly performed with high concentration of NPs in the presence of surfactant/ligand for reducing

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non-specific interactions, which is not a representative condition commonly encountered by filter membrane consumers.

NP enumeration techniques measure the optical, chemical, mechanical, or electrical characteristics of particles for their quantification. NP quantification by one of their properties usually limits their detection limit. As an example, one of the most sensitive techniques, inductively coupled plasma mass spectrometry (ICP-MS) that quantifies metal colloids by their mass has the detection limit of ~1E7 p/mL for 5 nm sized gold nanoparticle (GNP). In order to drastically enhance the detection limit of NPs, a novel approach/method would be needed. Application of ultrasensitive NP(s) in filter performance testing may provide a number of advantages including, lower NP challenge concentration for filter retention testing, better representation of customer application, and lower testing cost.

This work describes a new bio-surrogate method developed by Pall Corporation for evaluating particle retention performance of sub-15 nm nanoporous filter membranes. This method employs a novel DNA-dendrimer conjugate (referred as conjugate) developed by combining components from nanotechnology and biological sciences. A technique capable of single molecule detection is employed to detect sparse concentration of bio-surrogate providing >1000-fold higher detection sensitivity than any existing 5 nm-sized particle enumeration technique. Results demonstrate that this new DNA-dendrimer conjugate method can discriminate various sub-15 nm nanoporous filter membranes based on their retention performance. Due to ultrahigh detection sensitivity of DNA-dendrimer conjugate, lower challenge concentration of this conjugate (as compared to other NPs of this size) can be used for filter testing, producing a contaminant level that closely approximates the actual filter testing condition in customer applications.

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2. EXPERIMENTAL

2.1 DNA-dendrimer conjugate

Dendrimers are repetitively branched molecules, typically highly symmetric spherical compounds, and can be considered to have three major portions: a core, an inner shell, and an outer shell[3]. Dendrimers are classified by generation number, which refers to the number of repeated branching cycles that are performed during its synthesis. Dendrimers with size ranging from 2 nm to 20 nm, various functionalities, and applications are reported in literature[3]. Dendrimers also offer narrow size distribution, high stability, and chemical tunability. However, dendrimers have never being applied in filtration application. Direct detection of NP or dendrimer would provide limited detection sensitivity. For example, detection sensitivity of 5 nm GNP by one of the most sensitive techniques, ICP-MS is in the range of 1E6-1E7 p/mL. Therefore, our approach is based on detecting a tag (short DNA chain) attached to the NP and correlating the number of DNA tags to the number of NPs. This approach breaks the barrier of detection sensitivity of NP, or dendrimer in this case. Here a 5th generation polyamidoamine (PAMAM) dendrimer was reacted with a carboxylic terminated single-stranded DNA chain in a 1:1 ratio to synthesize DNA-dendrimer conjugate (Figure 1). Particle retention performance of filter membrane is only dependent on the size of dendrimer, which is approximately 5 nm in this case. DNA being flexible in nature does not impact retention performance. DNA-dendrimer conjugate was purified and was characterized for its monodispersity, amount of free-DNA, and filter membrane interaction. It was found that the conjugate remains monodispersed in basic aqueous buffer (pH 10.5), has <0.0005% free-DNA (can be applied to characterize filter membrane with >4-log reduction value particle retention performance), and does not interact with hydrophilic filter material such as nylon. Interaction of conjugate with hydrophobic filter material (e.g., polyethylene) was eliminated by including 0.03% Tween-20 in the challenge solution.

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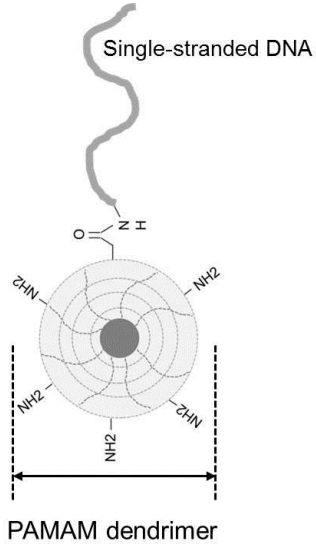

Figure 1. Schematic of a 5.4 nm DNA-dendrimer conjugate. A single stranded DNA chain (66 bases) is attached to the amino functionalized PAMAM dendrimer by an amide bond for producing a stable conjugate.

2.2 DNA-dendrimer conjugate quantification

DNA attached on the dendrimer was detected and quantified by quantitative polymerase chain reaction (qPCR). This biochemical reaction can amplify a single DNA chain into billions of chains under thermal cycling within 1-2 hours, providing real-time quantification of DNA chains in the sample[4]. The number of dendrimer particles can be calculated based on the number of DNA chains due to the 1:1 ratio of DNA and dendrimer on the conjugate.

DNA-dendrimer conjugate was diluted in basic aqueous buffer with the concentration of dendrimer ranging from 1E8 p/mL to 1000 p/mL. Diluted solutions were quantified by qPCR for evaluating the detection sensitivity of dendrimer particle. Figure 2 shows that qPCR was able to quantify 5 nm dendrimer particles up to the concentration of 2000 p/mL.

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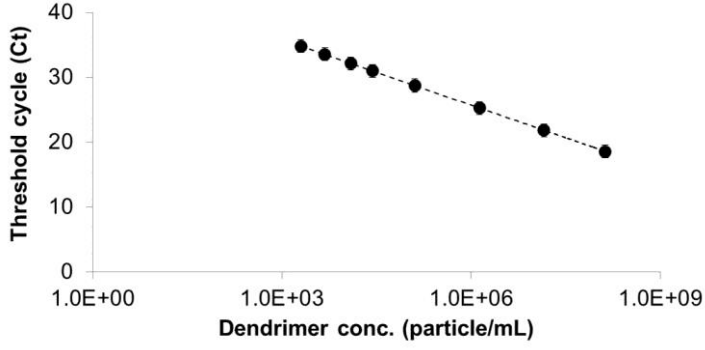

Figure 2. Dynamic range and sensitivity of detection of dendrimer by qPCR. Inverse relationship between qPCR threshold cycle with dendrimer concentration. This new method can detect and quantify 5 nm dendrimer particles up to a concentration of 2000 p/mL.

2.3 Filter Membrane

Two types of polymeric filter membranes with various pore-rating were evaluated. Commercially available filter membranes such as hydrophilic nylon and hydrophobic high density polyethylene (HDPE) were selected in this study due to their wide applications in microlithography for contaminant removal from process fluids. The main objective of this study was to test if the DNA-dendrimer conjugate testing method is capable of differentiating particle retention performance of hydrophilic and hydrophobic nanoporous filter membranes.

2.4 DNA-dendrimer conjugate challenge test

Conjugate challenge test was conducted in three steps as shown in Figure 3. In the step 1, test fluid (DNA-dendrimer conjugate in basic buffer solution with a concentration of C_o; 1E8 p/mL) was supplied through a 47-mm filter disc under air pressure at a constant flow rate of 5 mL/min. No ligand/surfactant was used with the hydrophilic nylon membrane testing, whereas 0.03% Tween-20 was applied in HDPE membrane testing to eliminate conjugate adsorption with the filter membrane. The initial 10 mL of permeate/effluent was discarded and the subsequent 10 mL of permeate (with a concentration of C_p) was collected for measurement. Challenge test was repeated three times (unless otherwise noted) to check the repeatability and reproducibility of the experiment. In the step 2, DNA attached to the dendrimer in both the challenge solution and filter permeate was quantified by qPCR. The number of DNA chains was directly correlated to the number of dendrimer particles due to

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1:1 ratio of DNA and dendrimer in the conjugate, providing the concentration of dendrimer in the challenge (C_o) and permeate (C_p) solutions. In the step 3, dendrimer retention performance of filter membrane was calculated by the inverse log of dendrimer concentration in the permeate solution by the dendrimer concentration in the challenge solution.

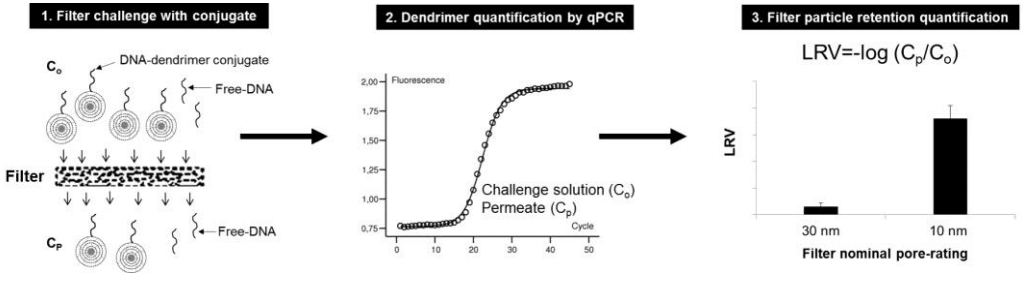

Figure 3. Schematic of DNA-dendrimer conjugate testing method. Testing is performed in 3 steps including, filter membrane challenge, dendrimer quantification by qPCR, and dendrimer retention performance quantification of filter membrane.

3. RESULTS AND DISCUSSION

3.1 Dendrimer retention performance of commercial nylon filter membranes

Figure 4 shows 5 nm dendrimer retention performances of nylon filter membranes with nominal pore-rating ranging from 40 nm to 5 nm. A consistent increase in the dendrimer retention performance with respect to decreasing pore-rating of filter membrane was observed. Very low retention/high passage of 5 nm dendrimer through 40 and 20 nm pore-rated nylon membrane (in the absence of any surfactant/ligand) confirmed low affinity of dendrimer conjugate to nylon polymer. Therefore, dendrimer removal by nanoporous nylon membrane may be greatly dominated by sieving effect as opposed to adsorptive effect. Additionally, this new conjugate method was able to discriminate 10 nm and 5 nm nominal pore-rated nylon membranes based on their dendrimer retention performances. Dendrimer (5 nm) retention performance of 5 nm pore-rated nylon membrane was approximately 3-fold higher than 10 nm pore-rated nylon membrane. Nylon filter membrane rating based on this new method can be correlated with the filter rating provided by GNP challenge testing[5]. Thus, nylon membrane ratings provided by this new conjugate method or GNP testing method can be used as guide for selecting the appropriate product in microlithography application.

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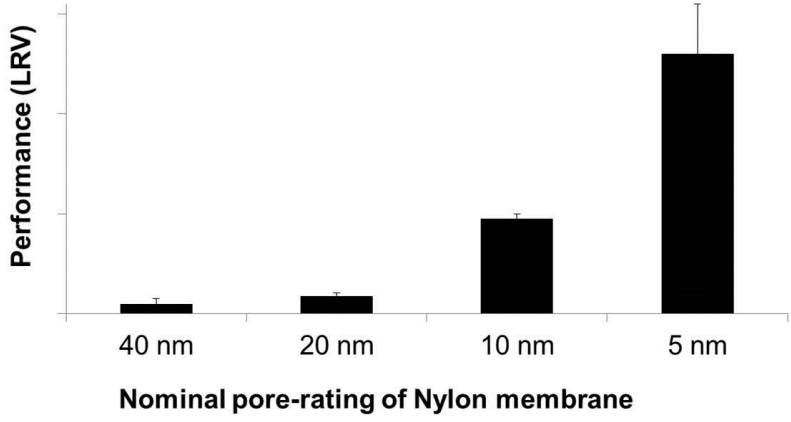

Figure 4. Dendrimer retention performance of various nominal pore-rated nylon filter membranes. Error bar is standard deviation of triplicate measurement. Conjugate test is capable of discriminating various nominal pore-rated nylon filter membranes.

3.2 Dendrimer retention performance of commercial HDPE filter membranes

Figure 5 shows 5 nm dendrimer retention performances of HDPE filter membranes with nominal pore-rating ranging from 30 nm to 2 nm. A consistent increase in the denderimer retention performance with respect to decreasing pore-rating of filter membrane was observed. Very low retention/high passage of 5 nm dendrimer through 30 pore-rated HDPE membrane (in the presence of 0.03% Tween-20) confirmed low affinity of dendrimer conjugate to polyethylene polymer. Therefore, dendrimer removal by nanoporous HDPE membrane may be greatly dominated by sieving effect as opposed to adsorptive effect. Additionally, this new conjugate method was able to discriminate 10 nm, 5 nm, and 2 nm nominal pore-rated HDPE membranes based on their dendrimer retention performance. Dendrimer (5 nm) retention performance of 2 nm pore-rated HDPE membrane was approximately 3-fold and 8-fold higher than 5 nm and 10 nm pore-rated HDPE membrane respectively. HDPE filter membrane rating based on this new method can be correlated with the filter rating provided by GNP challenge testing[5]. Thus, HDPE membrane ratings provided by this new conjugate method or GNP testing method can be used a guide for selecting the appropriate product in microlithography application.

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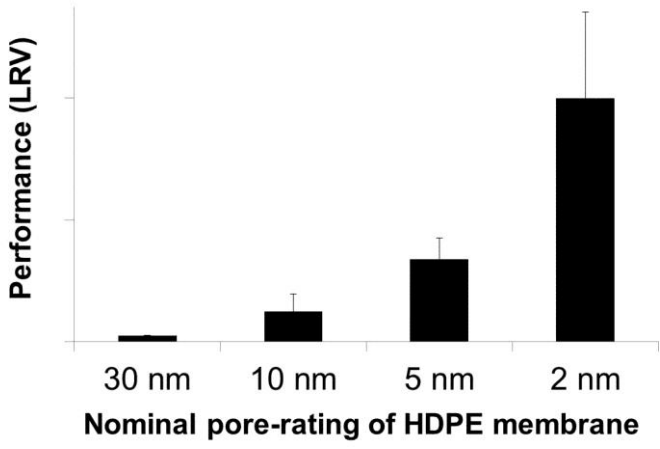

Figure 5. Dendrimer retention performance of various nominal pore-rated HDPE filter membranes. Error bar is standard deviation of triplicate measurement. Conjugate test is capable of discriminating various nominal pore-rated HDPE filter membranes.

3.3 Effect of dendrimer challenge concentration on retention performance of nylon membrane

Filter membranes get exposed to various concentrations of contaminants in microlithography applications. Therefore, it is very important to understand the impact of NP challenge concentration on particle retention performance of filter membrane. This understanding would be helpful in optimizing the NP challenge concentration in a new filter performance testing method. In general, nanoporous filter membrane testing requires 5 nm GNP with a concentration of ~5E10 p/mL for challenge testing, which cannot be reduced by a few orders of magnitude due to the detection sensitivity limitation of ICP-MS. Due to high detection sensitivity of our DNA-dendrimer conjugate, filter performance testing with various conjugate concentration was possible. Figure 6 shows the dendrimer retention performance of a 10 nm nominal pore-rated nylon membrane with respect to dendrimer challenge concentration ranging from 20,000 p/mL to 2E8 p/mL. Data shows that the conjugate challenge concentration over five-orders of magnitude range did not significantly impact the dendrimer retention performance of nylon membrane. It also indicates that nylon filter membrane can be applied to process fluids with either high or low contamination concentration. Even the highest challenge concentration of 5 nm dendrimer conjugate (2E8

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p/mL) is 250-fold lower than 5 nm GNP challenge concentration for GNP-based testing. Based on our knowledge, there is no 5 nm particle enumeration technique that could match the detection sensitivity of this new conjugate method. This bio-surrogate can mimic the contaminant level that closely approximates the actual filter testing condition in customer applications.

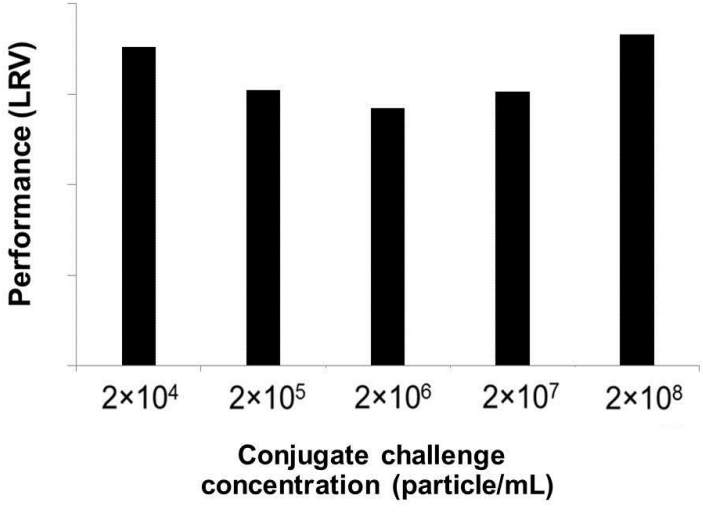

Figure 6. Dendrimer retention performance of 10 nm pore-rated nylon filter membrane with different challenge concentrations of conjugate. Nylon membrane performance is independent on dendrimer challenge concentration. Standard deviation of the LRVs is within the 10% of the mean LRV of all the tests.

4. CONCLUSION

A novel ultrasensitive biosurrogate for rating particle retention performance of nanoporous filter membranes below sub-15 nm nominal pore-rating was developed. This method utilizes a 5 nm DNA-dendrimer conjugate, which is detected (in the influent and effluent solutions) using qPCR, a single molecule-level sensitive technique. This method provides a detection sensitivity of 2000 p/mL, which is approximately 1000-fold higher than any existing 5 nm sized particle enumeration technique. Challenge testing of both hydrophilic (nylon) and

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hydrophobic (HDPE) filter membranes showed that this new conjugate method is capable of discriminating sub 15 nm-filters based on their nominal pore-rating. Data also showed that the conjugate challenge concentration over five-orders of magnitude range did not impact the dendrimer retention performance of 10 nm pore-rated nylon 6, 6 membrane. Therefore, nylon filter membrane can be applied to clean process fluids with either high or low contamination concentration, providing a better representation of filters in customer application. Application of this new conjugate method should provide better understanding of next generation filter membranes for removing defect-causing contaminants from microlithography processes.

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